shown schematically in Fig. 2(b) for the hypothetical case of an impurity giving rise to a p-wave resonance (this may apply to Sn in Na). It follows immediately from Eq. (2) that σ then becomes small whenever resonant (or bound) levels occur well below k_F. Thus, the appearance of giant diamagnetism automatically signals the disappearance of spin-flip scattering because phase shifts $\sim\pi$ near $k=0$ must decrease with k in order that the Friedel sum be satisfied at k_F.

In the case of noble-metal solvents, s and p levels must again emerge from the band bottom to cause a diamagnetism of high-valence impurities. It is possible that the one-electron levels are significantly broadened.[11] These phenomena will be discussed more fully in a future publication.

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Configuration Interaction in the X-Ray Photoelectron Spectra of Alkali Halides

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Satellites observed in the x-ray photoelectron spectra of the alkali halides are shown to arise from configuration interaction.

We have identified two-electron processes in the x-ray photoelectron spectra of alkali halides which are described by the final state of the excited atom and arise from configuration interaction. The observed effects are closely related to recently reported semi-Auger and radiative Auger satellites in soft-x-ray emission[1,2] and to some cases of electron "shake up."[3] The common feature of these experiments is the final state.

Satellites are produced whenever emission of either a photoelectron or an x ray is accompanied by the simultaneous excitation of another electron producing an atom with two inner-shell holes and one electron in an excited state. It is essential to distinguish between the intrinsic satellite structure resulting from this effect and the extrinsic structure due to energy loss suffered by the photoelectron as it leaves the crystal. Fortunately the electron energy-loss spectra of the alkali halides are well established.[4] Moreover, we have directly measured the energy-loss spectra for x-ray photoelectrons coming from our samples by exciting levels which should have no configuration-interaction satellites. The agreement between our observations and published data shows that the energy-loss spectra are very similar at 1.4 and 50 keV and help to avoid confusion between the two sources of satellite structure.[5]

Configuration-interaction satellites will be present in photoelectron spectra whenever there are other final states present with the same configuration (same total angular momentum and parity, or same total L and S in Russell-Saunders coupling) but somewhat greater binding energy than the single-hole final state. Perturbation theory further indicates that these other final states must have energies close to but greater than the single-hole final-state energy if the configuration-interaction satellites are to have reasonable intensities.[6] Final states with smaller binding energy tend to broaden the single-hole state through Coster-Kronig processes.[7] The conditions for observable configuration-interaction satellites are most readily met for the transition metals[8,9] and rare earths[10] where appropriate final states can be formed by a rearrangement of the electrons within unfilled $3d$ or $4f$ shells. In many other elements the energy differences may be too large and the orbital overlap too small to permit appreciable admixing of states. Such configuration-interaction satellites do occur for atoms near the inert gases, where appropriate two-hole final states can be formed with one electron promoted to an upper unoccupied energy level of the required symmetry.

The present experiments were carried out with freshly crushed powders of reagent-grade chemicals. These were mounted with double-sided scotch tape and measured slightly above room temperature in a Varian IEE 15 spectrometer with an aluminum-anode x-ray tube. The data shown have not been corrected for charging effects. To facilitate comparison with other work we give for each spectrum the measured position of the upper edge of the valence band obtained under identical experimental conditions. The experimental linewidth was ~2 eV.

The following compounds were investigated: LiCl, NaCl, KF, KCl, KBr, RbF, and RbCl. Identifiable configuration-interaction satellites were found for the Cl(3s) electrons in LiCl, the K(3s) electrons in all the potassium salts, and the Rb(4s) electrons in all the rubidium salts. Where possible a direct study of the energy-loss spectrum was made by examining the satellite structure of one or more electrons in the compound which have no configuration-interaction structure, e.g., the F(1s) and K(2s) electrons of KF. The good agreement between these data and the energy-loss spectra of Creuzburg[4] is illustrated in the insert in Fig. 1 for the case of RbF.

The x-ray photoelectron spectra in the region of the Rb(4s) energy level of the rubidium salts are shown in Fig. 1. The sharp line at 32.8 eV is due to the Rb(4s) electrons themselves [in the case of RbF the F(2s) line appears as a shoulder at 30.6 eV]. The shape of the energy-loss spectrum which is well established by auxiliary experiments (see inset) is shown as a dashed line. Its amplitude is taken to match the peak at 27.4 eV loss. The positions of the directly measured losses[4] are also shown. The broad line at ~10 eV below the Rb(4s) line is due to configuration interactions.

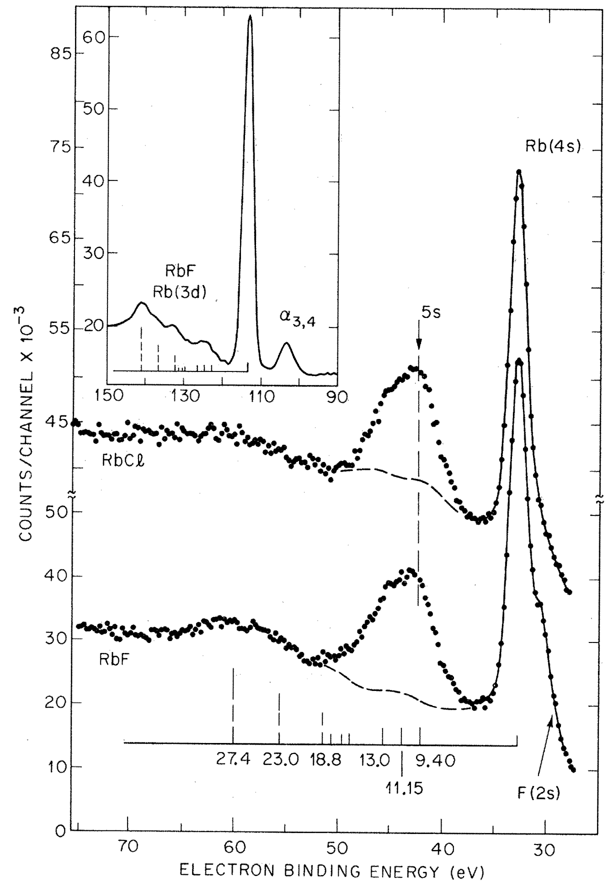

FIG. 1. Configuration-interaction satellites of the Rb(4s) electrons in RbF and RbCl. The discrete energy losses from Ref. 4 are also indicated. The inset shows the energy-loss tail of the Rb(3d) photoelectron spectrum of RbF. The heights of the dashed lines provide a *qualitative* indication of the strength of the discrete energy losses. The valence band edges are at 6.8 eV in RbF and 6.4 eV in RbCl.

Proof of this assertion is based in part on the elimination of other possibilities, i.e., that it is not a loss peak or a peak due to an impurity,[11] and in part on showing that it corresponds in position to the satellites computed from known atomic energy levels. Interaction is expected between the configurations $4s^14p^6\,{}^2S$ and $4s^24p^45s\,{}^2S$, whose energies[12] show that the latter is more tightly bound by 9.56 eV. The calculated position of this satellite is shown in Fig. 1 and corresponds to the dominant part of the observed structure. Another satellite with somewhat greater binding energy is expected for the configuration $4s^24p^44d\,{}^2S$. From our data we find that its binding energy is 12.5 eV in RbCl. In RbF it is less clearly resolved.

Data for three potassium salts are shown in

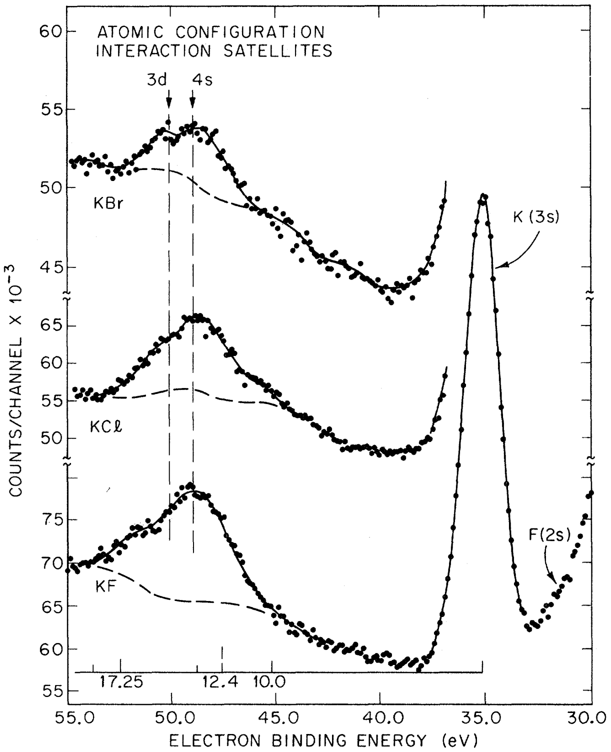

FIG. 2. Configuration-interaction satellites of the K(3s) electron in three potassium salts. The valence band edges were found at 7.6, 6.2, and 5.2 eV in KF, KCl, and KBr, respectively. Background has been subtracted.

Fig. 2. In this case both the $3s^2 3p^4 4s$ and $3s^2 3p^4 3d$ satellite positions are obtainable from Ref. 12 and correspond well to the details of the data for KBr and KCl. The data for KF suggest the presence of an additional satellite at higher binding energy, possibly due to the $3s^2 3p^4 4p\ ^2S$ configuration.

In the case of NaCl no satellite structure beyond that attributable to energy loss has so far been identified, perhaps because of smaller intensity. The relative strength of a satellite is apparently related to its separation from the parent line. The strongest satellites, found in the rubidium salts, also have the smallest separation from the parent line, ~10 eV. Their predicted position in sodium salts is ~20 eV below the Na(2s) line, making them much weaker by a perturbation theory argument. It should also be noted that the area of the satellite in the Rb salts is greater than that of the main line; i.e., configuration-interaction satellites involving final states with two holes in the same outer subshell following photoionization of this outer shell can be in some cases much more important than the "shake-off" effects following inner-shell excitation reported by Krause, Carlson, and Dismukes.[13]

The data on the K(3s) electron in KCl can be directly compared with those of Ref. 1. Since both deal with the same final state the good agreement between the two are both necessary and gratifying. The same configuration-interaction satellite has apparently also been observed in potassium metal by Crisp.[14] It is denoted by X in his paper and not further interpreted.

We have also observed the 6-eV satellite on the Cl(3s) line in LiCl which appears in the soft-x-ray spectrum of Fischer and Baun[15] and the semi-Auger work of Cooper and LaVilla.[1] [In KCl interference from the Al $K\alpha_{3,4}$ satellite of the K(3s) line makes observation of the Cl(3s) satellites more difficult.]

The x-ray photoelectron experiments reported here have succeeded in resolving structure in the configuration-interaction satellites in solids which were not obtained with the soft-x-ray technique. A major point of interest is that atomic calculations predict the satellite structure in solids so accurately. At first sight this appears strange since the 4s level of potassium makes up the conduction band of the potassium halides. It appears, however, that the ionized potassium of the final state must be thought of as a defect ion whose electronic levels are not part of the band structure. The 4s state will then be split off from the conduction band and appear in the gap. This would also explain why the same satellite is found even in the alkali metal.

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Photoluminescence of Amorphous $2As_2Te_3 \cdot As_2Se_3$ Films

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The photoluminescence of amorphous $2As_2Te_3 \cdot As_2Se_3$ films has been measured from 2 to 150°K with niobium-doped yttrium aluminum garnet laser excitation. The external quantum efficiency is estimated to be 20%. A typical spectrum consists of a broad band peaked at 0.61 eV with a half-width of 0.15 eV. The energy value for the luminescence peak supports the concept of a recombination gap in amorphous semiconductors.

On first thought luminescence seems to be highly unlikely in amorphous semiconductors: Though the existence of optical[1-5] and mobility[6,7] gaps is well established, at least for chalcogenides, the theory favors a continuum of states throughout the gap.[5-7] Thus, an electron excited into the conduction band is expected to give up its energy not by radiative recombination but rather by jumping down the continuum of states, by emitting phonons. In spite of that, photoluminescence has been found from bulk samples of amorphous $As_2Se_3 \cdot As_2Te_3$, As_2Se_3, and As_2S_3.[8,9] These luminescence spectra had maxima well below the forbidden gap and were attributed[8,9] to transitions to impurity-like levels within the quasiforbidden gap.

In this paper we present measurements of the photoluminescence from amorphous films of $2As_2Te_3 \cdot As_2Se_3$ and interpret the spectrum in terms of simultaneous radiative recombination and phonon emission in a continuum of states. We also give the first results for amorphous films and the first results on the temperature and excitation intensity dependence of the spectrum. We chose $2As_2Te_3 \cdot As_2Se_3$ since measurements of its photoconductivity[10] had led to the introduction of a new kind of gap for an amorphous semiconductor. The photoconductivity, though yielding two well-defined activation energies, could be explained on the basis of a continuous density of states throughout the forbidden gap by introducing recombination edges about 0.2 eV below the mobility edges.[10-12] Above the recombination edges, relaxation of excited carriers is more probable than recombination, and vice versa below the edges.[10] In consequence, the states below the recombination edges are not expected to be strongly populated with carriers created by incident light.

Experiment and results.—The films used were 0.5 to 1.0 μm thick and were obtained by electron beam heating of bulk material and condensing the vapor on sapphire substrates cooled to 77°K. The 1.06-μm radiation of the niobium-doped yttrium aluminum garnet (Nd:YAG) laser was chosen for excitation. Light of this wavelength penetrates about 0.4 μm into the sample,[13] far enough to keep surface effects low, but allowing a good fraction of the incident light to be absorbed. The area of the illuminated spot on the sample was about 4 mm^2, and laser intensities up to 400 mW were used. The luminescence was analyzed through a LiF prism monochromator with an effective slit width of about 0.04 eV at 0.6 eV, and detected by a PbS cell at ambient temperature. The laser was typically chopped at 80 Hz. No difference in the signal was found when the chopping frequency was reduced to 13 Hz, which indicates that all detectable recombinations occur in a time much less than 10 msec. The excitation intensity was varied by calibrated metal-film filters. For measure-